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Trapping volatile nitrosamines with copper incorporated zeolites†

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Modification of zeolite with copper oxide significantly promotes the selectively adsorption of volatile nitrosamines, beneficial for the removal of nitrosamines in cigarette smoke.

Volatile nitrosamines (VNA) in mainstream cigarette smoke are carcinogenic and their removal is difficult. Although zeolite NaY can adsorb more VNA than NaZSM-5 and NaA,[1] adding NaY catalysts in the cigarette blend only reduces by 5–10% the *N*-nitrosodimethylamine (NDMA) in the mainstream.[2] Ordered mesoporous materials like SBA-15 and MCM-48 are more active for degradation of bulky *N′*-nitrosonornicotine, yet their capacity for selectively adsorbing VNA is rather smaller.[3] Therefore, novel materials are sought to eliminate VNA and a new strategy should be adopted besides choosing the pore structure of the adsorbent. Monocyclic nitrosamines such as *N*-nitrosopyrrolidine (NPYR) usually have a planar structure because of the large rotational barriers of their N–NO bonds,[4] and they may adsorb on zeolite because of the way the –N–N=O groups insert into the zeolite channels.[3] Thus, all of the methods accelerating the adsorption of NOx on zeolite will be beneficial for adsorption of nitrosamines. Since the incorporation of copper species in zeolite was helpful for adsorption of nitrous oxide,[5] we designed and prepared new trapping composites through a simple impregnation method, resulting in improved efficiency for selective adsorption of VNA.

NDMA, NPYR and *N*-nitrosohexamethyleneimine (NHMI), purchased from Sigma, were dissolved in methylene chloride; zeolites NaY, NaZSM-5 and SBA-15 were used as adsorbent.[3] Copper was incorporated in the porous support using ‘drying impregnation’ with $Cu(NO_3)_2$,[6] and the concentration of aqueous solution was controlled to give different loading of copper cations. The resulting samples were characterized by using XRD, XRF[5] and XPS.[7] Adsorption of VNA was performed in a micro-reactor filled with 5 mg of sample in which the nitrosamine solution was pulse injected at 453 K.[1] Gaseous effluent was analyzed by an on-line Varian 3380 gas chromatograph, and the decrement in the ratio of solute to solvent utilized to calculate the amount adsorbed.[3] IR tests were carried out using a Bruker 22 FT-IR spectrometer. The sample disc (15 mg cm^{-2}) located in an *in situ* cell[8] was activated in N_2 at 773 K for 2 h then brought into contact with NPYR at 453 K.

Figure 1A shows the influence of loading CuO on the capacity of zeolite NaY for selective adsorption of NPYR; 3 wt.% was proven to be the best amount of loading. More NPYR can be selectively adsorbed on the sample of 3% CuO/NaY without interference of organic solvent in comparison with the parent zeolite, though the surface area of the former (770 m^2 g^{-1}) was smaller than the latter (859 m^2 g^{-1}). In the case that the total amount of NPYR arrived at 3.0 mmol g^{-1}, 75.0% of the carcinogenic compound could be adsorbed by 3% CuO/NaY, meanwhile 56.8% adsorbed on NaY. When 5.60 mmoles of NPYR passed through the adsorbents, about half (52.7%) was adsorbed on the former whereas 39.3% was adsorbed by the latter. Promotion by copper was also observed in the selective adsorption of NDMA, the typical VNA with the smallest molecular size. Zeolite NaZSM-5 is known to adsorb less NDMA than NaY under the same conditions.[1,9] However, a loading of 3 wt.% CuO on NaZSM-5 made this difference disappear, indicating a new way to promote the adsorption of VNA on zeolite through chemical modification. As further proof for this inference, a 5% CuO/SBA-15 sample adsorbed more NHMI than SBA-15, as illustrated in Fig. 1B. For instance, 24.9% of the adsorbate was adsorbed on the former at the total amount of 0.40 mmol g^{-1} while 15.7% was adsorbed on the latter. This difference increases as the total amount of NHMI reaches 0.70 mmol g^{-1}, 21.7% of it can be adsorbed on the former but only 12.1% on the latter.

Figure 2 illustrates the difference spectra of NPYR adsorbed on zeolite NaY and CuO/NaY. This is the first reported IR spectrum of nitrosamines adsorbed on zeolite. 1458, 1371 and 1306 cm^{-1} bands are observed on the spectrum of NaY, similar to that of $\nu_3(NO_2)$ (ν_3 = 1470–1450 cm^{-1}), nitro species[10] and C–N vibration reported in the standard spectrum of NDMA. However, different IR bands appeared on the spectra of CuO/NaY. The band at 2212 cm^{-1} can be assigned to the isolated nitrosonium ion and that at 2134 cm^{-1} results from NO_2^+ species located on copper ions or NO_2 adsorbed on Cu^{2+} ion.[11] As the loading of CuO increases to 5 wt.%, the band centered at 1616 cm^{-1} which originates from the adsorbed NO_2^- reaches its maximum.[5] Besides the N=O vibration band around 1454 cm^{-1}, the 1422 cm^{-1} band of nitrito complex[12] is also observed, accompanied by the weak bands at 1383 cm^{-1}, one of the characteristic bands of pyrrolidine (PYR), and 1322 cm^{-1} whose ascription is not clear yet. Through the comparison of spectrum *d* with *a*–*c* in Fig. 2, it is clear that NPYR adsorbed on CuO/NaY sample in fact has undergone a different interaction

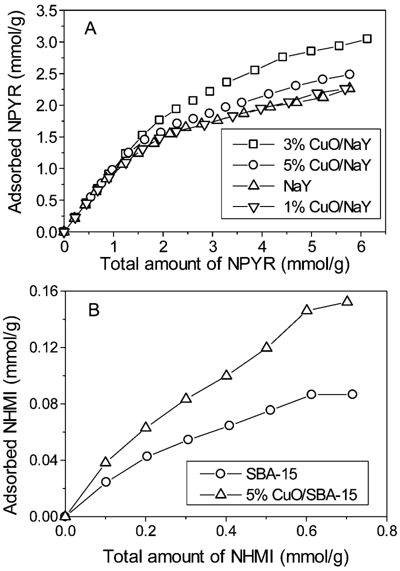

Fig. 1 Influence of loading copper on the selective adsorption of NPYR (upper) over zeolite NaY and NHMI (lower) on SBA-15 at 453 K.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b304322c/

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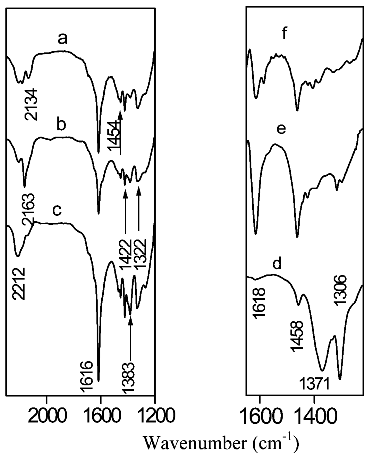

Fig. 2 FT-IR spectra of NPYR adsorbed on (a) 1% CuO/NaY, (b) 3% CuO/NaY, (c) 5% CuO/NaY and (d) NaY zeolite, and PYR adsorbed on (e) NaY zeolite and (f) 3% CuO/NaY sample at 453 K.

with the adsorbent and degrades at 453 K to form fragments that include nitrogen oxides and PYR. To confirm this assumption, PYR was also adsorbed on both zeolite NaY and 3% CuO/NaY under the same conditions. However, the spectra obtained are almost same as demonstrated in Fig. 2. Both NPYR and PYR molecules have a five-membered ring structure, the only difference being that the former has an –N–N=O functional group while the latter has –N–H. That means, the –N–N=O functional group of nitrosamines has a strong interaction with the copper species dispersed on zeolite NaY so that the carcinogenic compounds can be more easily selectively adsorbed and decomposed on the CuO/NaY sample. Thus, modifying the zeolites with metal species like copper oxides will elevate the efficiency for trapping nitrosamines, especially for removal of VNA in cigarette smoke.

To evaluate the effect of zeolite for removing VNA in smoke, 16 Virginia type cigarettes (tar of 15 mg per cigarette and nicotine of 1.3 mg per cigarette) were machine smoked under the standard ISO conditions.[13] The mainstream smoke first passes through the adsorption column containing 0.5 g zeolite, then passes the citrate-phosphate buffer solution including 20 mM ascorbic acid to absorb the residual nitrosamines in the smoke. The total amount of nitrosamines in the buffer is determined by spectrophotometric method.[8] Figure 3 illustrates the removal of nitrosamines from mainstream cigarette smoke by use of adsorbents. Although the MS smoke passes through the cigarette filter and the Cambridge pad of the smoking machine, there still remains a considerable amount of nitrosamines in it (2.36 nmol per cigarette). Adsorption by zeolite NaY eliminates 47% of the carcinogenic compounds and the residual content lowers to 1.24 nmol per cigarette. Modification with copper obviously increases the efficiency of NaY for removing VNA as seen in Fig. 3. The residual nitrosamines in the buffer solution decrease to 1.04, 0.72 and 0.85 nmol per cigarette as the MS smoke passes through the sample of 1% CuO/NaY, 3% CuO/NaY and 5% CuO/NaY respectively, which means that about 56%, 69% and 64% of nitrosamines are indeed removed. To confirm the existence of the nitrosamines trapped in the composite, the used adsorbent of 3% CuO/NaY was examined by XPS spectroscopy[7,14] and about 2.65% of N-containing species were detected on the surface whereas no N1s signal was observed on a fresh sample. Besides, more than 100 nmol per g of nitrosamines are released from the sample in a TPD process from 373 K to 773 K, providing further proof of the adsorption. Incorporation of copper also makes the siliceous SBA-15 much more efficient in adsorbing nitrosamines, 72% of the nitrosamines in MS smoke can be removed by the sample of 5% CuO/SBA-15 whereas about 50% is eliminated by SBA-15. Since the pore size of SBA-15 is tremendous (8 nm) in comparison with VNA, the copper species incorporated (5 wt.%) cannot significantly reduce the pore size of the adsorbent to create optimized adsorbate–adsorbent interaction as is often observed in zeolites. The enhanced ability in selective adsorption of VNA can but result from some effects between nitrosamines and copper. That means, some materials located in the zeolite will attract the –N–N=O function group of nitrosamines so that the adsorption can thus be accelerated, though the mechanism still needs to be explored in detail.

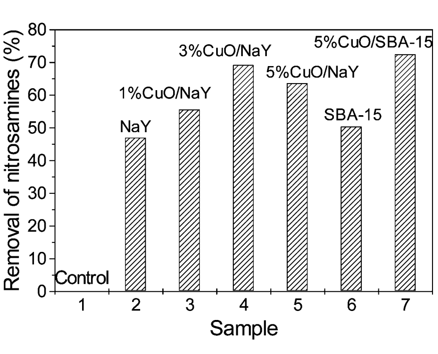

Fig. 3 Removal of nitrosamines in the mainstream smoke of cigarette by use of zeolite NaY and SBA-15 modified with CuO.

The selective adsorption of carcinogenic compounds is a key step in the removal of pollutants from the environment and so increasing the selectivity of the adsorbent materials is highly desirable. Compared to adjusting the pore structure of the adsorbent, a low-cost and timesaving method is to change the surface property of zeolite and mesoporous materials by using chemical modification, in order to increase the adsorbate–adsorbent interaction and to make novel trapper materials for the protection of public health and life.

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Notes and references

1 B. Shen, L. L. Ma, J. H. Zhu and Q. H. Xu, *Chem. Lett.*, 2000, **29**, 380.
2 W. M. Meier and K. Siegmann, *Microporous Mesoporous Mater.*, 1999, **33**, 307.
3 J. H. Zhu, S. L. Zhou, Y. Xu, Y. Cao and Y. L. Wei, *Chem. Lett.*, 2003, **32**, 338.
4 M. Miura, S. Sakamoto, K. Yamaguchi and T. Ohwada, *Tetrahedron Lett.*, 2000, **41**, 3637.
5 J. Szanyi and M. T. Paffett, *J. Catal.*, 1996, **164**, 232.
6 J. L. Dong, J. H. Zhu and Q. H. Xu, *Appl. Catal. A: General*, 1994, **112**, 105.
7 J. Despres, M. Koebel, O. Krocher, M. Elsener and A. Wokaun, *Microporous Mesoporous Mater.*, 2003, **58**, 175.
8 J. H. Zhu, J. L. Dong, J. Zhang, P. X. Hu and Q. H. Xu, *Acta Chimica Sinica.*, 1995, **53**, 111.
9 J. H. Zhu, D. Yan, J. R. Xia, L. L. Ma and B. Shen, *Chemosphere*, 2001, **44**, 949.
10 M. Sirilumpen, R. T. Yang and N. Tharapiwattananon, *J. Mol. Catal. A: Chemical.*, 1999, **137**, 273.
11 K. Hadjiivanov, J. Saussey, J. L. Freysz and J. C. Lavalley, *Catal. Lett.*, 1998, **52**, 103.
12 C.-C. Chao and J. H. Lunsford, *J. Am. Chem. Soc.*, 1971, **93**, 71.
13 International Organisation for Standardisation (1991) ISO 3308: Routine analytical cigarette-smoking machine – Definition and standard condition.
14 J. H. Zhu, Y. Wang, Y. Chun and X. S. Wang, *J.C.S. Faraday Trans.*, 1998, **94**, 1163.